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(71) Applicant (for all designated States except US): **CYTEC TECHNOLOGY CORP.** [US/US]; 300 Delaware Avenue, Wilmington, DE 19801 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **ROBERTSON, Allan, James** [CA/CA]; 36 Forster Avenue, Thorold, Ontario L2V 4J5 (CA).

(74) Agents: **DIDAMO, Valerie, T.** et al.; Cytec Industries Inc., 1937 West Main Street, P.O. Box 60, Stamford, CT 06904-0060 (US).

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(54) Title: PHOSPHONIUM SALTS

(57) Abstract: The invention provides a phosphonium salt of formula I wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are C<sub>1-20</sub> hydrocarbyl groups and X is an anion, except halide, provided that (i) R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are not all the same; and (ii) not more than two of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are aryl. Such phosphonium salts may be useful as catalysts, solvents, and electrolytes.

## Phosphonium Salts

### Field of the Invention

This invention relates to phosphonium salts and  
5 particularly to such salts in the form of ionic liquids.

### Background of the Invention

Ionic liquids are salts that are liquid over a broad range of temperatures. Ionic liquids are useful for many purposes, including as catalysts, solvents, and electrolytes<sup>10</sup> (for a general review, see Olivier, H. (1998), "Nonaqueous Ionic Liquids (NAILs)", in Aqueous Phase Organometallic Catalysis Concepts and Applications, Wiley-VCH, Chapter 7.3, pp. 554-563). Known ionic liquids are generally nitrogen-based systems. For example, U.S. Patent No. 5,731,101 (March 24,  
15 1998; Sherif et al.) describes compositions comprising mixtures of a metal halide, such as aluminum trichloride ( $\text{AlCl}_3$ ), and an alkyl-containing amine hydrohalide salt, such as trimethylamine hydrochloride salt ( $(\text{CH}_3)_3 \text{NH}^+\text{Cl}^-$ ) to form an ionic liquid, such as  $(\text{CH}_3)_3\text{NH}^+\text{Al}_2\text{Cl}_7^-$ . Pyridinium salts are  
20 described by Chum et al (J. Am. Chem. Soc., 97, 3264 (1975)).

Other examples of ionic liquids include 1-ethyl-3-methylimidazolium tetrachloroaluminate and 1-butylpyridinium nitrate (Chemical & Engineering News, March 30, 1998, pages 32 to 37), and dialkylimidazolium chloroaluminates (Wilkes, J.S.  
25 et al. "Dialkylimidazolium chloroaluminate melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis" Inorg. Chem., 21, 1263-1264 (1982)).

Phosphonium salts have been previously described.  
30 For example, U.S. Patent No. 5,310,853, (May 10, 1994; Pham et al) describes phosphonium catalysts for use in fast cures of

epoxy resins. However, the phosphonium salts of the examples are not ionic liquids.

#### Summary of the Invention

In one aspect, the invention provides a phosphonium salt of formula I:



wherein

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> each independently represents a C<sub>1-20</sub> hydrocarbyl group, provided that (i) R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are not all the same; and (ii) no more than two of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are aryl, and

X<sup>-</sup> is an anion, excluding halide.

#### Description of the Preferred Embodiments of the Invention

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and X<sup>-</sup> are preferably chosen to obtain low melting salts. If the salt is to be used as a polar solvent for an organic reaction, then there should be chosen a salt whose melting point is below the temperature at which the reaction is to be carried out.

In general it is preferred that the phosphonium salt of the invention is a liquid below 100°C, more preferably a liquid below 50°C, most preferably a liquid below 35°C.

The melting point of the phosphonium salt depends mostly upon the particular hydrocarbyl groups that are attached to the phosphorus atom. For instance, a higher number of carbon atoms present tends to result in a lower melting product. Branching also tends to result in a lower melting product, so it is preferred that alkyl groups are branched, for

example,  $\alpha$ -branched or  $\beta$ -branched. Steric considerations may limit this, for instance, and may prohibit salts in which all of R<sup>1</sup> to R<sup>4</sup> are  $\alpha$ -branched. Branching is especially preferred when the anion is a tosylate. Choosing R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> such 5 that they are not all the same also tends to lower the melting point of the salt.

The hydrocarbyl groups R<sup>1</sup> to R<sup>4</sup> are preferably alkyl groups but they may be, or contain, aryl groups such as phenyl, tolyl, or naphthyl groups. They may be alicyclic groups such 10 as cyclopentyl or cyclohexyl groups. They are preferably free of ethylenic unsaturation. Further, the hydrocarbyl groups may be substituted. Suitable substituents include hydroxyl and halides.

The hydrocarbyl groups can be interrupted by 15 heteroatoms that do not interfere with the utility of the phosphonium salts, or the carbon chain can bear non-interfering substituents. Which heteroatoms or which substituents interfere, of course, depends on the intended utility of the phosphonium salt and will therefore vary from case to case. 20 Oxygen is mentioned as a heteroatom that can be present in a carbon chain.

The total number of carbon atoms present in R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> is chosen with many factors in mind but is usually 7 to 30, preferably 22 to 26 and more preferably 24.

25 Preferably, one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> is a C<sub>8-20</sub> alkyl group, more preferably a C<sub>10-16</sub> alkyl group.

For some purposes, it is desirable that at least one of R<sup>1</sup> to R<sup>4</sup> is a long chain alkyl group containing a straight chain of at least 14 carbon atoms.

4

Preferably, when X is tosylate, at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> is a branched alkyl group, and two, three, or all four can be branched.

Partially fluorinated ethers are one class of R groups which can be particularly useful in certain applications. Phosphonium salts comprising one or more of such R groups tend to have high densities (for example, 1.3 to 1.5), making them well suited for phase separation. The partially fluorinated ethers may also be further substituted. An example of a partially fluorinated ether is -(CH<sub>2</sub>)<sub>m</sub>-O-CH<sub>2</sub>(CF<sub>2</sub>)<sub>n</sub>CF<sub>3</sub> wherein n represents a number from 0 to 9, preferably 4, 6, or 8, and m represents a number from 1 to 6, preferably 3.

Other specific examples of suitable R groups include hydroxyalkyl groups, such as 3-hydroxypropyl.

As well as being able to vary the melting points of the phosphonium salts of the invention to suit various purposes, the miscibility of the phosphonium salts with organic compounds can be extensively varied, particularly by altering the chain lengths of the R groups. This feature can be quite useful in carrying out a chemical reaction. For instance, in a reaction where the salt is used as a polar solvent, the salt may be selected because it is miscible with a product of the reaction at elevated temperature but immiscible at a lower temperature. In this example, upon termination of the reaction, the reaction mixture can be cooled to the lower temperature to result in two liquid phases and the product phase simply decanted off. This lower temperature is preferably ambient temperature. Alternatively, if the salt is miscible with the product at the lower temperature, one possibility to separate the product from the salt is to boil off the product, leaving the solvent ready to be used again. In general, the longer the hydrocarbyl groups are, the greater

the miscibility with organic reactants and products. With shorter hydrocarbyl groups, the product and/or reactant may become miscible with the phosphonium salt upon heating.

The phosphonium salt can be selected with the  
5 required properties as a solvent in mind.

As there are four groups, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup>, that can be varied, the phosphonium salts display a high degree of flexibility that assists in selecting particular properties of the salt, such as the melting point. This contrasts, for  
10 instance, with the known imidazolium salts mentioned above, which have only two groups that can be varied. It also contrasts with ammonium salts. Although ammonium salts bear four groups attached to one nitrogen atom, in practice the ammonium salts are made from tertiary amine precursors, and it  
15 is difficult to make mixed tertiary amines. Hence the ammonium salts that are practically available are confined to those which have three identical and one different group attached to the nitrogen atom, so their flexibility is limited.

It is not difficult to prepare phosphonium salts  
20 bearing different groups, giving a higher degree of flexibility. Tertiary phosphines can be prepared by reacting phosphine with an olefin or a mixture of olefins. For example, if phosphine is reacted with a mixture of hexene and octene there is obtained a mixture of four tertiary phosphines,  
25 namely, trihexyl, trioctyl, dihexyloctyl and dioctylhexyl phosphines. This provides additional flexibility in tailoring the tertiary phosphine and, subsequently, the phosphonium salt to have particular selected properties.

Suitable anions, X, include phosphate, nitrate,  
30 hexafluorophosphate (PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>), tetrafluoroborate, (BF<sub>4</sub><sup>-</sup>) tetrachloroaluminate (AlCl<sub>4</sub><sup>-</sup>), Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>, carboxylates, and

sulfonates. Examples of sulfonates include tosylate, mesylate, benzenesulfonate, and triflate. Examples of carboxylates include acetate, propionate, and trifluoroethanoate. Preferred anions are sulfonates, tetrafluoroborate, hexafluorophosphate, 5  $\text{SbF}_6^-$ ,  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$ . Especially preferred are tosylate, tetrafluoroborate, and hexafluorophosphate.

The anion, X, also affects the properties of the phosphonium salt, including the melting point. Many anions are available but the required properties of the phosphonium salt 10 should be borne in mind when selecting the anion.

As examples of liquid phosphonium salts there are mentioned triisobutylmethylphosphonium tosylate and diisobutyl-n-octylmethylphosphonium tosylate, both of which are liquids at room temperature. The compound tri-n-butylmethyl-phosphonium 15 tosylate is a high melting solid. The distinction in melting point between the tri-n-butyl compound and the corresponding triisobutyl compound is a clear demonstration of the effect of branching on the melting point of the compound.

Ionic liquids of the invention are also suitably 20 formed from mixtures of phosphonium salts of formula I.

The phosphonium sulfonates of the invention can readily be prepared by reacting a tertiary phosphine  $\text{R}^1\text{R}^2\text{R}^3\text{P}$  with a sulfonate ester  $\text{R}^4\text{X}$ , where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are as defined above, and X is a sulfonate. A mixture of different 25 tertiary phosphines can be used. The reaction proceeds readily at elevated temperature, say 60 to 100°C, and is often complete in about 4 to 5 hours. For instance, phosphonium tosylates are readily prepared by heating a tertiary phosphine with a tosylate ester, suitably a lower alkyl tosylate ester, to form 30 a phosphonium tosylate.

In cases where the anion is other than a sulfonate, it is convenient to first prepare the corresponding halide salt, by combining a tertiary phosphine  $R^1R^2R^3P$  with an alkyl halide under conditions similar to those given above for 5 tosylates. For instance, there may readily be prepared a phosphonium chloride, by reaction of a tertiary phosphine with a lower alkyl chloride.

Phosphonium hexafluorophosphates and tetrafluoroborates are typically prepared through an anion 10 exchange process from a halide salt such as the chloride or bromide salt.

In some instances it is convenient to then convert the phosphonium halide, by anion exchange, to the desired phosphonium salt. For instance, to prepare phosphonium 15 hexafluorophosphate or tetrafluoroborate from the phosphonium chloride, an anion exchange is done with the corresponding phosphonium chloride and hexafluorophosphoric acid, e.g. in a 60% aqueous solution in water as solvent, or sodium tetrafluoroborate in acetone as solvent. To make the 20 carboxylate, phosphate, sulfate, nitrate, or acetate salts, the corresponding phosphonium chloride is mixed with sodium hydroxide in methanol. Sodium chloride falls out of solution. The resulting phosphonium hydroxide is mixed with the acid corresponding to the desired salt (i.e. a carboxylic acid is 25 used to form a phosphonium carboxylate) to obtain the desired product.

To form the tetrachloroaluminate, a phosphine is mixed with trichloroaluminum.

Trace levels of halide ion usually remain in the 30 phosphonium salt when converting a phosphonium halide to another salt. If such converted salts are to be used in an

environment where halide ions are unacceptable, even at low levels, phosphonium halides should not be used as starting materials, or a process must be used which ensures complete removal of halide ions. For instance, halide ions such as

5 chloride ions coordinate with group VIII metals such as palladium and platinum. If the phosphonium salt is to be used as a solvent for a reaction that is catalysed by a palladium or platinum catalyst the phosphonium salt must be totally free of halide anion. Sulfonates would be preferred in such cases.

10 Halide ions do not coordinate with nickel, so if the phosphonium salt is to be used as a solvent for a nickel-catalysed reaction it is acceptable that trace levels of halide ion remain.

The phosphonium salts of the invention are very

15 thermally stable. They have extremely low vapour pressure and may decompose rather than boil. The temperature at which this occurs will vary from compound to compound, but substantially all are stable up to about 200°C, many are stable up to about 300°C and some are stable even up to about 450°C. These

20 properties render them useful for many purposes, but particularly for use as a solvent for various reactions including carbonylation, hydrogenation, hydroformylation, olefin dimerization, olefin oligomerization, olefin polymerization, acylation, alkylation, reduction and oxidation

25 reactions. For instance the reaction of carbon monoxide, ethylene and methanol or ethanol in the presence of a palladium catalyst to form methyl acetate or ethyl acetate, respectively, can be carried out in a phosphonium salt of the invention as solvent, and the product ester distilled off thereafter.

30 The invention is further illustrated in the following examples.

**Example 1**Preparation of triisobutylethylphosphonium tosylate:

An inerted reactor was charged with ethyl tosylate. After heating the tosylate ester to 100-110°C, a 2-3% molar excess of 5 triisobutylphosphine was added slowly over 1-2 hours. The reaction was exothermic and the temperature of the reaction was controlled by regulating the addition rate and by removing the source of heat. After a two hour digestion period the mixture was cooled to 50°C at which point enough dilute aqueous 10 hydrogen peroxide was added to convert the excess triisobutylphosphine (less than 0.5%) to the corresponding phosphine oxide. The product mixture was then vacuum stripped to remove the water. The triisobutylethylphosphonium tosylate product was a solid (mp 28-29°C) but it could be supercooled 15 and thus remain a liquid at 10-12°C. Above 30°C, it was a viscous liquid and its viscosity decreased rapidly with increasing temperature. It was more dense than water (approximately 1.06 g/cc at 30°C).

**Example 2**Preparation of triisobutylmethylphosphonium tosylate:

The procedure of Example 1 was followed, except that methyl tosylate was used in place of ethyl tosylate. The triisobutylmethylphosphonium tosylate product that was obtained from the vacuum stripping was a viscous liquid at room 25 temperature but its viscosity decreased rapidly with increasing temperature. Its density was approximately 1.065/cc at 30°C.

## Examples 3 to 12

Alkylphosphonium tosylates listed in Table 1 were synthesized in a manner similar to that described for Examples 1 and 2.

Table 1: Alkyl Phosphonium Tosylates

Example	<u>R<sup>1</sup></u>	<u>R<sup>2</sup></u>	<u>R<sup>3</sup></u>	<u>R<sup>4</sup></u>	<u>m.p.</u> <u>(C)</u>	<u>Density (g/mL)</u>	
						<u>30°C</u>	<u>60°C</u>
8	Et	Et	Et	Et	68-69	-	-
9	n-Pr	n-Pr	n-Pr	Me	50-52	0.9974	0.9802
10	n-Pr	n-Pr	n-Pr	Et	52-53	-	-
11	n-Bu	n-Bu	n-Bu	Me	72-73	-	-
12	n-Bu	n-Bu	n-Bu	Et	71.5-	-	-
					73.5		
2	iBu	iBu	iBu	Me	liquid <sup>2</sup>	1.0664	1.0486
1	iBu	iBu	iBu	Et	28-29	1.0593	1.0416
3	iBu	iBu	octyl	Me	<40	1.0229	1.0036
4	iBu	iBu	octyl	Et	liquid <sup>2</sup>	1.0148	0.9955
5	iBu	iBu	tetrade cyl	Me	<40	0.9885	0.9681
6	iBu	iBu	tetrade cyl	Et	liquid <sup>2</sup>	0.9821	0.9619
7	Mixed Hexyl/Octyl <sup>1</sup>			Me	<40	0.9853	0.9661

5

<sup>1</sup>The phosphonium salts were prepared from a mixture of phosphines ( $R^1R^2R^3P$ ), wherein  $R^1$ ,  $R^2$ , and  $R^3$  are each hexyl or octyl.

10

<sup>2</sup>At Room Temperature.

**Example 13**

Preparation of tri-hexyl(tetradecyl)phosphonium hexafluorophosphate: 202 g of tri-hexyl(tetradecyl)phosphonium chloride was dissolved in 293 g of distilled water. To this 5 solution 99.4 g of 60% aqueous hexafluorophosphoric acid was added with stirring at room temperature. A waxy immiscible solid formed. After two hours of stirring, the mixture was warmed to 45°C. At this point there were two liquid layers. The aqueous layer was decanted and the organic phase was washed 10 two times with two volumes of distilled water at 45°C to remove residual HCl. Finally the organic phase was heated to 100°C under 20 mmHg pressure to remove the last traces of water. 238 g of a low melting (29-33°C) product was recovered.

**Examples 14 to 21**

15 Alkylphosphonium hexafluorophosphates listed in Table 2 were synthesized in a manner similar to that described for Example 13. Example 21 is provided for the purpose of comparison.

Table 2: Alkyl Phosphonium Hexafluorophosphates

<u>Example</u>	<u>R<sub>1</sub></u>	<u>R<sub>2</sub></u>	<u>R<sub>3</sub></u>	<u>R<sup>4</sup></u>	<u>m.p. (C)</u>	<u>P NMR (ppm)</u>		<u>F NMR (ppm)</u>	
						<u>R<sub>4</sub>P</u>	<u>PF<sub>6</sub></u>	<u>R<sub>4</sub>P</u>	<u>PF<sub>6</sub></u>
16	Propyl	Propyl	Propyl	Tetradecyl	44.5-45.5	32.46	-143.67	-69.22	-73.02
15	Butyl	Butyl	Butyl	Tetradecyl	38.0-39.0	33.75	-143.54	-69.83	-73.61
14	Pentyl	Pentyl	Pentyl	Tetradecyl	35.5-37.0	33.55	-143.68	-69.18	-72.97
13	Hexyl	Hexyl	Hexyl	Tetradecyl	29-33	33.53	-143.68	-69.93	-73.7
21	Butyl	Butyl	Butyl	Butyl	161-163	34.47	-143.32	-70.47	-74.25
17	Dodecyl	Dodecyl	Dodecyl	Dodecyl	72-78	33.2	143.47	-69.5	-73.28
18	Mixed Butyl/Hexyl <sup>1</sup>			Tetradecyl	liquid/solid <sup>2</sup>	33.4	-143.75	-69.89	-73.67
19	Mixed Butyl/Octyl <sup>1</sup>			Butyl	<30	34.36	-143.36	-70.45	-74.21
20	Mixed Hexyl/Octyl <sup>1</sup>			Octyl	55.5-64.0	33.45	-143.85	-70.11	-73.39

<sup>1</sup>The phosphonium salts were prepared from a mixture of phosphines (R<sup>1</sup> R<sup>2</sup> R<sup>3</sup>P), wherein R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each one of the two components listed.

<sup>2</sup>At Room Temperature.

**Example 22**

Preparation of tri-hexyl(tetradecyl)phosphonium tetrafluoroborate: A stirred reactor was charged with two parts of acetone and one part by weight of tri-hexyl (tetradecyl)phosphonium chloride. To this solution was added a 50% molar excess of sodium tetrafluoroborate. The mixture was stirred vigorously for 10 minutes at room temperature. Afterwards, it was filtered to remove the excess sodium tetrafluoroborate and precipitated sodium chloride. The clear acetone solution containing tri-hexyl(tetradecyl)phosphonium tetrafluoroborate was then heated under reduced pressure to remove the acetone. The final conditions were 140°C at 0.3 mmHg pressure. The product was slightly viscous pale yellow oil which had a melting point of 30°C. The chloride content was 0.16%. This represents approximately 98% conversion of the chloride to tetrafluoroborate.

**Examples 23 and 24**

Alkylphosphonium tetrafluoroborates listed in Table 3 were synthesized in a manner similar to that described for Example 22.

Table 3: Alkyl Phosphonium Tetrafluoroborates

<u>Examples</u>	<u>R<sub>1</sub></u>	<u>R<sub>2</sub></u>	<u>R<sub>3</sub></u>	<u>R<sub>4</sub></u>	<u>m.p. (C)</u>	<u>P NMR (ppm)</u> <u>R<sub>4</sub>P</u>	<u>F NMR (ppm)</u> <u>BF<sub>4</sub></u>	<u>B NMR (ppm)</u> <u>BF<sub>4</sub></u>
23	Butyl	Butyl	Butyl	Tetradecyl	32-35	33.83	-153.74	-0.7224
22	Hexyl	Hexyl	Hexyl	Tetradecyl	liquid <sup>2</sup>	33.32	-149.09	-1.021
24	Mixed Butyl/Hexyl <sup>1</sup>			Tetradecyl	liquid	33.45		-1.1602

1The phosphonium salts were prepared from a mixture of phosphines (R<sub>1</sub> R<sub>2</sub> R<sub>3</sub>P), wherein R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are each butyl or hexyl.

2At Room Temperature.

**Example 25**

Preparation of diisobutyl(methyl)(3-(1,1-dihydroperfluoroctoxy)propyl)phosphonium tosylate: A stirred reactor was charged with one equivalent of methyltosylate.

5 After heating the tosylate ester to 100°C, one equivalent of diisobutyl(3-(1,1-dihydroperfluoroctoxy)propyl)phosphine was added over 2 hours. The mixture was held for an additional 6 hours at 100°C. The product was a viscous liquid at room temperature, with a density and viscosity of 1.34 g/cc and 5.8  
10 cps, respectively, at 60°C.

**Example 26**

Preparation of bis(3-(1,1-dihydroperfluoroctoxy)propyl)(isobutyl)(methyl)phosphonium tosylate: A stirred reactor was charged with one equivalent of methyltosylate.

15 After heating the tosylate ester to 100°C, one equivalent of bis(3-(1,1-dihydroperfluoroctoxy)propyl)(isobutyl) phosphine was added over 2 hours. The mixture was held for an additional 6 hours at 100°C. The product was a viscous liquid at room temperature, with a density and viscosity of 1.5 g/cc and 50  
20 cps, respectively, at 60°C.

**Example 27**

The miscibility of phosphonium iodides with dodecane as a function of number of carbons in a series of phosphonium iodides was determined. While phosphonium iodides are not part 25 of the claimed invention, this example is provided here to demonstrate how miscibility may be affected by carbon number for phosphonium salts. The first column of Table 4 identifies the tertiary phosphine, most of which have R groups which are a mixture of different lengths. Column 2 identifies the alkyl  
30 iodide with which the tertiary phosphine has been reacted to form a phosphonium iodide. Column 3 shows the average number

of carbon atoms per phosphonium iodide molecule and column 4 shows the average molecular weight of the phosphonium iodide products. The last column shows the temperature at which the phosphonium iodide became miscible with dodecane.

5 This Table demonstrates that the miscibility of the phosphonium iodides with dodecane decreases as the number of carbon atoms in the phosphonium iodide increases.

Table 4: Miscibility of Phosphonium Iodides with Dodecane

R <sup>3</sup> P	R <sup>1</sup>	Carbon No.	Ave. Mwt.	MP (C)	Miscib. Temp
C <sub>6</sub> /C <sub>8</sub> <sup>1</sup>	C <sub>4</sub>	24.9	506.6	Liquid <sup>2</sup>	>162
C <sub>6</sub> /C <sub>8</sub> <sup>1</sup>	C <sub>6</sub>	26.9	534.6	Liquid <sup>2</sup>	>162
C <sub>6</sub> /C <sub>8</sub> <sup>1</sup>	C <sub>8</sub>	30.9	590.6	Liquid <sup>2</sup>	162
C <sub>6</sub> /C <sub>8</sub> <sup>1</sup>	C <sub>10</sub>	32.9	618.6	Liquid <sup>2</sup>	132
C <sub>8</sub> /C <sub>12</sub> <sup>1</sup>	C <sub>4</sub>	33.5	627	31	125
C <sub>10</sub> /C <sub>12</sub> <sup>1</sup>	C <sub>4</sub>	34.8	645.2	27	102
C <sub>8</sub> /C <sub>12</sub> <sup>1</sup>	C <sub>6</sub>	35.5	655	42	110
C <sub>8</sub> /C <sub>12</sub> <sup>1</sup>	C <sub>8</sub>	37.3	680.2	54	71
C <sub>10</sub> /C <sub>12</sub> <sup>1</sup>	C <sub>6</sub>	38.8	701.2	42	83
C <sub>10</sub>	C <sub>10</sub>	40	718	Liquid <sup>2</sup>	57
C <sub>12</sub>	C <sub>4</sub>	40	718	Liquid <sup>2</sup>	43
C <sub>12</sub>	C <sub>6</sub>	42	746	Liquid <sup>2</sup>	34
C <sub>12</sub> /C <sub>14</sub> <sup>2</sup>	C <sub>4</sub>	42.8	757.2	46	37

<sup>1</sup>The phosphonium salts were prepared from a mixture of phosphines (R<sup>1</sup> R<sup>2</sup> R<sup>3</sup>P), wherein R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each one of the two components listed.

5   <sup>2</sup>At Room Temperature

CLAIMS:

1. A phosphonium salt of formula I



5 wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are C<sub>1</sub>-20 hydrocarbyl groups and X is an anion, excluding halide, provided that

- (i)  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are not all the same; and
- (ii) not more than two of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are aryl.

2. The salt according to claim 1, wherein the sum total  
10 of the carbon atoms present in  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  is from 7 to 30 inclusive.

3. The salt according to claim 1 or 2, wherein at least two of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are different from the others of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ .

15 4. The salt according to claim 1, 2, or 3, wherein one of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  includes a straight chain of 14 or more carbon atoms.

5. The salt according to any one of claims 1 to 4, wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are all saturated acyclic groups.

20 6. The salt according to any one of claims 1 to 5, wherein at least one of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  is a partially fluorinated ether.

7. The salt according to claim 6, wherein at least one of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  is  $-CH_2CH_2CH_2-O-CH_2(CF_2)_nCF_3$ , wherein n  
25 is 4, 6, or 8.

8. The salt according to any one of claims 1 to 7, wherein at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> is a hydroxyalkyl group.

9. The salt according to claim 8, wherein at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> is 3-hydroxypropyl.

10. The salt according to any one of claims 1 to 5, wherein the anion is selected from the group consisting of sulfonates, tetrafluoroborate, hexafluoroborate, SbF<sub>6</sub><sup>-</sup>, AlCl<sub>4</sub><sup>-</sup>, and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>.

11. The salt according to any one of claims 1 to 10 having a melting point below 100°C.

15 12. The salt according to any one of claims 1 to 10 having a melting point below 50°C.

13. The salt according to any one of claims 1 to 10 having a melting point below 35°C.

20

14. Use of a phosphonium salt according to any one of claims 1 to 13 as a reaction solvent.

## INTERNATIONAL SEARCH REPORT

Application No  
PCT/US 01/12780

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07F9/54

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	LUDLEY P ET AL: "Phosphonium tosylates as solvents for the Diels-Alder reaction" TETRAHEDRON LETTERS, vol. 42, no. 10, 4 March 2001 (2001-03-04), pages 2011-2014, XP004238666 ISSN: 0040-4039 Salts A and B	1-3, 5, 10-14
X	COMYNS, CLAIRE ET AL: "Clean catalysis with clean solvents - phosphonium tosylates for transfer hydrogenation reactions" CATALYSIS LETTERS, vol. 67, no. 2-4, 2000, pages 113-115, XP001008262 ISSN: 1011-372X the whole document	1-3, 5, 10-14

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*&\* document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Elliott, A

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International Application No  
PCT/US 01/12780

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KARODIA ET AL: "Clean catalysis with ionic solvents - phosphonium tosylates for hydroformylation" CHEMICAL COMMUNICATIONS, no. 21, 1998; pages 2341-2342, XP002172927 ISSN: 1359-7345 Salt 4 ---	1-3,5, 10-14
X	BOY CORNILS (EDITOR), WOLFGANG A. HERMANN (EDITOR): "Aqueous Phase Organometallic Catalysis, Concepts and Applications" 28 May 1998 (1998-05-28), WILEY-VCH XP001007486 ISBN: 3527294783 cited in the application page 555 -page 563 ---	1-14
X	ABDALLAH, DAVID J. ET AL: "Smectic Liquid-Crystalline Phases of Quaternary Group VA (Especially Phosphonium) Salts with Three Equivalent Long n-Alkyl Chains. How Do Layered Assemblies Form in Liquid-Crystalline and Crystalline Phases?" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 122, no. 13, 5 April 2000 (2000-04-05), pages 3053-3062, XP002172924 ISSN: 0002-7863 table 1 ---	1,3-5, 10-13
X	ESTERUELAS, MIGUEL A. ET AL: "Reductive Elimination of 'Ph <sub>2</sub> C:C:CHPR <sub>3</sub> !BF <sub>4</sub> from the Rhodium(III)-Allenyl Derivatives 'Rh(acac){CH:C:CPh <sub>2</sub> }(PR <sub>3</sub> ) <sub>2</sub> !BF <sub>4</sub> (PR <sub>3</sub> = PCy <sub>3</sub> , PiPr <sub>3</sub> )" ORGANOMETALLICS, vol. 16, no. 21, 14 October 1997 (1997-10-14), pages 4572-4580, XP002172925 ISSN: 0276-7333 Compounds 9 and 13 ---	1-3, 10-13
X	IMRIE, C. ET AL: "Photolysis of (aryl methyl)triphenylphosphonium salts. Substituent, counterion, and solvent effects on reaction products" JOURNAL OF ORGANIC CHEMISTRY, vol. 58, no. 21, 1993, pages 5643-5649, XP001007323 ISSN: 0022-3263 Compound (5) ---	1-3, 10-13
		-/-

## INTERNATIONAL SEARCH REPORT

Application No  
PCT/US 01/12780

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KANAZAWA, AKIHIKO ET AL: "Polymeric phosphonium salts as a novel class of cationic biocides. II. Effects of counter anion and molecular weight on antibacterial activity o polymeric phosphonium salts" JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY, vol. 31, no. 6, 1993, pages 1441-1447, XP001007322 ISSN: 0887-624X Compounds (2), (3) and (4) ---	1-3, 10-13
X	DEMA, ANNE C. ET AL: "Transformation of alkynylphosphine oxides and alkynylphosphonium cations to 2-alkylidene-1,2-dihydro-3-phosphete ligands by platinum-hydrogen addition and rearrangement reactions" ORGANOMETALLICS, vol. 10, no. 4, 1991, pages 1197-1200, XP001007321 ISSN: 0276-7333 page 1198, compounds 5a and 5b ---	1-3, 10-13
X	JONES, RICHARD A. ET AL: "Synthesis and x-ray crystal structure of (triphenylmethyl)trimethylphosph nium tetrafluoroborate" JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS II, no. 1, 1980, pages 117-120, XP001007320 abstract ---	1-3, 10-13
X	EP 0 640 646 A (TEIJIN LTD) 1 March 1995 (1995-03-01) example 12 ---	1-5, 10-13
X	CERICHELLI ET AL: "Role of Counterions in the Catalytic Activity and Phase Equilibria of Phosphonium Salts in Water" LANGMUIR, vol. 16, no. 1, 11 January 2000 (2000-01-11), pages 166-171, XP002172929 ISSN: 0743-7463 the compound CTBPN03 ---	1-5, 11-13
		-/-

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/12780

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ALBANESE D ET AL: "Synthesis of Pentacoordinated Tetraalkylammonium and Tetraalkylphosphonium Difluorosilicates" TETRAHEDRON LETTERS, vol. 36, no. 48, 27 November 1995 (1995-11-27), pages 8865-8866, XP004026854 ISSN: 0040-4039 compound 3f	1-5, 11-13
X	MASATSUGU OGATA ET AL: "EFFECTS OF CROSSLINKING ON PHYSICAL PROPERTIES OF PHENOL-FORMALDEHYDE NOVOLAC CURED EPOXY RESINS" JOURNAL OF APPLIED POLYMER SCIENCE, vol. 48, no. 4, 20 April 1993 (1993-04-20), pages 583-601, XP000455203 ISSN: 0021-8995 table II	1-5, 10-13
X	US 4 867 790 A (JOCHUM PETER ET AL) 19 September 1989 (1989-09-19) example 13; table 2	1-3,5, 10-13
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 365 (C-532), 29 September 1988 (1988-09-29) -& JP 63 119490 A (DAI ICHI KOGYO SEIYAKU CO LTD), 24 May 1988 (1988-05-24) abstract	1-5,8-13
X	US 3 976 566 A (PETROVICH VOJISLAV) 24 August 1976 (1976-08-24) examples 1,3,4,7,8,11-13,16,18,19,24,25,27,28	1-3,5,8, 9,11-13
X	US 4 837 394 A (ALEXANDROVICH PETER S ET AL) 6 June 1989 (1989-06-06) column 8, line 35 - line 36	1-3,8-13
X	EP 0 455 257 A (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY INC) 6 November 1991 (1991-11-06) examples 2,7	1-3,5,8, 11-13
X	EP 0 161 128 A (EASTMAN KODAK CO) 13 November 1985 (1985-11-13) page 5, compounds 10 & 12	1-3,8-13
		-/-

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/12780

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VANMAELE L: "Non-polymeric phosphonium mordanting agents" RESEARCH DISCLOSURE, no. 287, 1988, pages 133-134, XP001008612 ISSN: 0374-4353 the whole document ---	1-4, 11-13
X	KHASKIN ET AL: "Organic insectofungicides. Thione-thiol isomérisation of quaternary phosphonium 0,0-dialkylthiophosphates" ZHURNAL OBŞHCHEI KHIMII, vol. 38, no. 12, 1968, pages 2652-2658, XP001008399 ISSN: 0044-460X the whole document ---	1-4, 11-13
X	BARRAUD A ET AL: "A NOVEL HIGHLY CONDUCTING PHOSPHONIUM TETRACYANOQUINODIMETHANE LANGMUIR-BLODGETT FILM" THIN SOLID FILMS, vol. 160, no. 1 + INDEX, 1 June 1988 (1988-06-01), pages 81-85, XP000024752 ISSN: 0040-6090 figure 1 ---	1-5, 11-13
A	ADAMS ET AL: "Friedel-Crafts reactions in room temperature ionic liquids" CHEMICAL COMMUNICATIONS, no. 19, 1998, pages 2097-2098, XP002172928 ISSN: 1359-7345 the whole document ---	1-14
A	CHAUVIN, YVES ET AL: "Catalytic dimerization of alkenes by nickel complexes in organochloroaluminate molten salts" JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, no. 23, 1990, pages 1715-1716, XP001007301 ISSN: 0022-4936 Page 1716, Table 1, Entry 9 ---	1-14
		-/-

## INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/12780

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BOHM, VOLKER P. W. ET AL: "Coordination chemistry and mechanisms of metal-catalyzed C-C coupling reactions; Part 12 nonaqueous ionic liquids: superior reaction media for the catalytic Heck -vinylation of chloroarenes" CHEMISTRY - A EUROPEAN JOURNAL, vol. 6, no. 6, 17 March 2000 (2000-03-17), pages 1017-1025, XP002172926 ISSN: 0947-6539 Table 1, Entry 7 ---	1-14
A	CHAUVIN, YVES ET AL: "Catalytic dimerization of olefins by nickel complexes in organochloroaluminate molten salts" ELECTROCHEMICAL SOCIETY PROCEEDINGS, PROCEEDINGS OF THE 7TH INTERNATIONAL SYMPOSIUM ON MOLTEN SALTS, vol. 90, no. 17, 1990, pages 822-832, XP001008355 ISSN: 0161-6374 the whole document ---	1-14
A	CHAUVIN Y ET AL: "OLIGOMERIZATION OF N-BUTENES CATALYZED BY NICKEL COMPLEXES DISSOLVED IN ORGANOCHLOROALUMINATE IONIC LIQUIDS" JOURNAL OF CATALYSIS, US, ACADEMIC PRESS, DULUTH, MN, vol. 165, 1997, pages 275-278, XP002070945 ISSN: 0021-9517 the whole document ---	1-14
A	FISCHER T ET AL: "Diels-Alder Reactions in Room-Temperature Ionic Liquids" TETRAHEDRON LETTERS, NL, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, vol. 40, no. 4, 22 January 1999 (1999-01-22), pages 793-796, XP004151448 ISSN: 0040-4039 the whole document --- -/-	1-14

## INTERNATIONAL SEARCH REPORT

In: International Application No  
PCT/US 01/12780

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WESSOLOWSKI, HOLGER ET AL: "Novel perfluoroalkenylphosphonates and iodoperfluoroalkenes from 3,3-bis(trifluoromethyl)-1,2,2,4,4,4-hexafluoro-1-butylene and nonafluoro-n-butoxy-1,1,2-trifluoroethylene"</p> <p>JOURNAL OF FLUORINE CHEMISTRY, vol. 80, no. 2, 1996, pages 149-152, XP004071323 ISSN: 0022-1139 Compounds 5a and 5b</p> <p>-----</p>	6,7

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No	
PCT/US 01/12780	

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 0640646	A	01-03-1995		JP 7062077 A JP 7126374 A JP 7165905 A JP 3071641 B JP 8059975 A US 5486555 A US 5494952 A US 5668202 A		07-03-1995 16-05-1995 27-06-1995 31-07-2000 05-03-1996 23-01-1996 27-02-1996 16-09-1997
US 4867790	A	19-09-1989		DE 3702233 A AT 70969 T DE 3867248 A EP 0279238 A JP 63201107 A		04-08-1988 15-01-1992 13-02-1992 24-08-1988 19-08-1988
JP 63119490	A	24-05-1988		JP 2039945 C JP 7062021 B		28-03-1996 05-07-1995
US 3976566	A	24-08-1976		NONE		
US 4837394	A	06-06-1989		NONE		
EP 0455257	A	06-11-1991		US 5030766 A AU 653934 B AU 7635991 A BR 9101796 A CA 2041840 A CN 1056865 A JP 5117186 A PL 290134 A US 5225387 A		09-07-1991 20-10-1994 07-11-1991 17-12-1991 05-11-1991 11-12-1991 14-05-1993 27-01-1992 06-07-1993
EP 0161128	A	13-11-1985		US 4496643 A CA 1252666 A DE 3568226 D JP 60213960 A		29-01-1985 18-04-1989 16-03-1989 26-10-1985